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(21) International Application Number: PCT/US96/17526 (22) International Filing Date: 1 November 1996 (01.11.96) (30) Priority Data: 60/012,021 21 February 1996 (21.02.96) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CICHA, Walter, Vladimir [CA/US]; Apartment 4C, 502 Red Fox Lane, Newark, DE 19711-5973 (US). MANZER, Leo, E. [US/US]; 714 Burnley Road, Wilmington, DE 19803-1729 (US). (74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: PHOSGENE MANUFACTURING PROCESS (57) Abstract A process for producing phosgene is disclosed which involves contacting a mixture comprising CO and Cl ₂ (e.g., at about 300 °C or less) with carbon having an active metal content of less than 1000 ppm by weight and a high degree of oxidative stability (i.e., a weight loss of about 12 percent, or less, in the WVC Temperature Test as defined herein).		

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TITLE

PHOSGENE MANUFACTURING PROCESS

FIELD OF THE INVENTION

5 This invention relates to a process for the manufacture of phosgene by the reaction of chlorine with carbon monoxide in the presence of a carbon catalyst. More particularly, this invention relates to a process for the manufacture of phosgene with minimal production of the hazardous chemical, carbon tetrachloride.

BACKGROUND

10 The production of phosgene by the reaction of chlorine with carbon monoxide in the presence of a carbon catalyst is a well known process. The phosgene produced by this process will typically contain 400 to 500 ppm by weight carbon tetrachloride. This amount, evaluated on the basis of the total world-wide production of phosgene of about ten billion pounds (4.5×10^9 kg) corresponds to co-production of about 4 to 5 million pounds (1.8×10^6 kg to 2.3×10^6 kg) of
15 carbon tetrachloride with the phosgene.

Japanese patent publication (Kokoku) No. Hei 6[1994]-29129 discloses that the amount of carbon tetrachloride produced during the phosgene manufacturing process can be reduced (e.g., by about 50%) by using an activated carbon which has been washed with an acid and which contains a total of
20 1.5 wt. % or less of metal components comprised of transition metals, boron, aluminum and silicon.

Carbon tetrachloride has been of concern in connection with ozone depletion and global warming potentials. Therefore, there is an interest in developing phosgene processes in which the amount of carbon tetrachloride
25 impurity is minimized.

SUMMARY OF THE INVENTION

A process for producing phosgene is provided which comprises contacting a mixture comprising carbon monoxide and chlorine with carbon. In accordance with this invention, the carbon (1) has an active metal content of less than
30 1000 ppm by weight, and (2) loses about 12% of its weight, or less, when sequentially heated in air for the following times and temperatures; 125°C for 30 minutes, 200°C for 30 minutes, 300°C for 30 minutes, 350°C for 45 minutes, 400°C for 45 minutes, 450°C for 45 minutes and finally at 500°C for 30 minutes. Typically the contact is at a temperature of about 300°C, or less.

DETAILED DESCRIPTION

35 The present invention relates to improving the production of phosgene produced by contacting carbon monoxide and chlorine with carbon. The improvement can be employed in connection with any of those carbon-based

processes used commercially or described in the art (e.g., those processes disclosed in U.S. Patent Nos. 4,231,959 and 4,764,308).

Phosgene is commercially manufactured by passing carbon monoxide and chlorine over activated carbon. The reaction is strongly exothermic and is usually
5 done in multitubular reactors to more effectively control the reaction temperature. Carbon monoxide is typically added in at least a stoichiometric amount (often in stoichiometric excess) to minimize the free chlorine content of the phosgene product.

As used in connection with this invention, the term "active metals" means
10 metals included in the group consisting of transition metals of groups 3 to 10, boron, aluminum and silicon. Carbon which contains less than about 1000 ppm by weight of active metals is employed. Iron is considered a particularly harmful active metal (i.e., the greater the amount of iron the larger the amount of carbon tetrachloride produced). It is preferred to use carbons which not only have an
15 active metal content of less than about 1000 ppm by weight, but also contain less than about 100 ppm by weight of iron (and more preferably less than about 80 ppm by weight iron). It is also preferable to use carbons which contain less than 200 ppm by weight of sulfur and less than 200 ppm by weight of phosphorus (and more preferably less than 100 ppm by weight each, of phosphorus and sulfur).

20 The carbons used for the process of this invention also exhibit substantial weight stability when heated in air. More particularly, when heated in air at 125°C for 30 minutes, followed by heating at 200°C for 30 minutes, followed by heating at 300°C for 30 minutes, followed by heating at 350°C for 45 minutes, followed by heating at 400°C for 45 minutes, followed by heating at 450°C for 45 minutes and
25 finally followed by heating at 500°C for 30 minutes, the carbons employed for the process of this invention lose about 12% of their weight, or less. This sequence of time and temperature conditions for evaluating the effect of heating carbon samples in air is defined herein as the "WVC Temperature Test". The WVC Temperature Test may be run using thermal gravimetric analysis (TGA). Carbons which when
30 subjected to the WVC Temperature Test lose about 12% of their weight, or less, are considered to be advantageously oxidatively stable.

Carbon from any of the following sources are useful for the process of this invention; wood, peat, coal, coconut shells, bones, lignite, petroleum-based residues and sugar. Commercially available carbons which may be used in this
35 invention include those sold under the following trademarks: Barneby & Sutcliffe™, Darco™, Nuchar™, Columbia JXN™, Columbia LCK™, Calgon PCB™, Calgon BPL™, Westvaco™, Norit™ and Barnaby Cheny NB™. The carbon support can be in the form of powder, granules, or pellets, or the like.

Preferred carbons include acid-washed carbons (e.g., carbons which have been treated with hydrochloric acid or hydrochloric acid followed by hydrofluoric acid). Acid treatment is typically sufficient to provide carbons which contain less than 1000 ppm of active metals. Suitable acid treatment of carbons is described in
5 U.S. Patent No. 5,136,113.

Particularly preferred carbons include three dimensional matrix porous carbonaceous materials. Examples are those described in U.S. Patent No. 4,978,649, which is hereby incorporated by reference herein in its entirety. Of note are three dimensional matrix carbonaceous materials which are obtained by
10 introducing gaseous or vaporous carbon-containing compounds (e.g., hydrocarbons) into a mass of granules of a carbonaceous material (e.g., carbon black); decomposing the carbon-containing compounds to deposit carbon on the surface of the granules; and treating the resulting material with an activator gas comprising steam to provide a porous carbonaceous material. A carbon-carbon composite
15 material is thus formed.

The carbon surface area as determined by BET measurement is preferably greater than about 100 m²/g and more preferably greater than about 300 m²/g.

It is known from dissociation equilibria that at 100°C, phosgene contains about 50 ppm chlorine; and that at 200°C, about 0.4%, at 300°C, about 5% and at
20 400°C about 20% of the phosgene is dissociated into carbon monoxide and chlorine. Also, the higher the reaction temperature, the more carbon tetrachloride is generally produced. Accordingly, the temperature of the reaction is generally about 300°C, or less (e.g., in the range of from 40°C to 300°C). Preferably, the temperature of the process is from about 50°C to 200°C; more preferably from
25 about 50°C to 150°C. The phosgene produced by the process of this invention typically contains about 300 ppm by weight or less of carbon tetrachloride, based upon phosgene (i.e., 300 parts by weight CCl₄ per million parts by weight COCl₂, or less) even at a temperature of 300°C. Preferably, the reaction temperature and the carbon are chosen to provide phosgene which contains less than about
30 250 ppm by weight of carbon tetrachloride; and more preferably, are chosen to provide phosgene which contains less than about 100 ppm by weight of carbon tetrachloride, based upon phosgene. Of note are embodiments where the reaction time and temperature are controlled to provide a carbon tetrachloride concentration of about 100 ppm or less based upon the total product stream.

35 Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely

illustrative, and does not constrain the remainder of the disclosure in any way whatsoever.

EXAMPLES

General Catalyst Testing Procedure

5 A 1/2" (1.27 mm) O.D. x 15" (381 mm) Inconel® 600 nickel alloy tube containing a 100 mesh (0.015 mm) Monel® nickel alloy screen was used as the reactor. The reactor was charged with about 2.5 mL to about 8 mL of carbon catalyst and heated to 300°C. This was the temperature used for all the examples.

 A 1:1 molar ratio mixture of carbon monoxide and chlorine was passed
10 over the catalyst. The contact times were between 8 to 12 seconds. The experimental results are shown in Table 1.

 The comparative examples were done in the same way as described above. The results are shown in Table A.

General Analytical Procedure

15 The reactor effluent was sampled on-line with a Hewlett Packard HP 5890 gas chromatograph using a 105 m long, 0.25 mm I.D. column containing Restak™ RTX-1 Crossbond 100% dimethyl polysiloxane. Gas chromatographic conditions were 50°C for 10 minutes followed by temperature programming to 200°C at a rate of 15°C/minute. The smallest amount of carbon tetrachloride that could be
20 quantitatively identified was about 80 ppm by weight.

Thermal Analysis Procedure

 Thermal gravimetric analysis (TGA) was done using a TA Instruments analyzer. The TGA experiments were done in air at a flow rate of 80 mL/min. The carbon sample was heated in air for the following times and temperatures;
25 125°C for 30 minutes, 200°C for 30 minutes, 300°C for 30 minutes, 350°C for 45 minutes, 400°C for 45 minutes, 450°C for 45 minutes and finally at 500°C for 30 minutes. The weight loss was measured at each interval and finally after completion of the heating cycle. The percentage weight loss after completion of the heating cycle at 500°C is shown in the tables.

Legend

Carbon Sample

- A-D. Porous carbonaceous material.
- E. HCl and HF washed sample of coconut shell carbon.
- R. Commercial sample (1) of coconut shell carbon.
- 35 S. HCl washed sample of Carbon Sample R.
- T. Commercial sample (2) of coconut shell carbon.
- V. Calcined petroleum coke.

TABLE 1

Ex.	Carbon Sample	CCl ₄ Conc. ¹ ppm	CCl ₄ Conc. ² ppm	TGA Wt. Loss ³ wt. %	Active Metal Content ⁴ ppm	Fe Content ppm	Surface Area m ² /g
1	A	100	161	0.86	27	13	-
2	E	100	158	9.63	125	21	-
3	B	90	140	1.15	358	28	350
4	C	90	139	9.15	836	64	409
5	D	<50	<90	3.37	516	37	500

¹ By weight as ppm of the product stream. The values shown are averages taken over 7 hours and are high-end estimates.

² By weight as ppm of the phosgene produced. The values shown are averages taken over 7 hours and are high-end estimates.

³ The carbon sample was heated in air for the following times and temperatures; 125°C for 30 minutes, 200°C for 30 minutes, 300°C for 30 minutes, 350°C for 45 minutes, 400°C for 45 minutes, 450°C for 45 minutes and finally at 500°C for 30 minutes.

⁴ Active metals consist of transition metals of groups 3 to 10, boron, aluminum and silicon.

Comparative Examples

TABLE A

Ex.	Carbon Sample	CCl ₄ Conc. ¹ ppm	CCl ₄ Conc. ² ppm	TGA Wt. Loss ³ wt. %	Active Metal Content ⁴ ppm	Fe Content ppm	Surface Area m ² /g
A	S	400	640	14.94	659	81	-
B	R	320	500	89.83	4900	360	1012
C	T	220	340	88.20	1516	130	835
D	V	120	320	7.54	2934	50	0.58

¹ By weight as ppm of the product stream. The values shown are averages taken over 7 hours and are high-end estimates.

² By weight as ppm of the phosgene produced. The values shown are averages taken over 7 hours and are high-end estimates.

³ The carbon sample was heated in air for the following times and temperatures; 125°C for 30 minutes, 200°C for 30 minutes, 300°C for 30 minutes, 350°C for 45 minutes, 400°C for 45 minutes, 450°C for 45 minutes and finally at 500°C for 30 minutes.

⁴ Active metals consist of transition metals of groups 3 to 10, boron, aluminum and silicon.

CLAIMS

What is claimed is:

1. A process for producing phosgene, comprising:
contacting a mixture comprising CO and Cl₂ at about 300°C or less
5 with carbon having an active metal content of less than 1000 ppm by weight and a
weight loss of about 12 percent, or less, in the WVC Temperature Test.
2. The process of Claim 1 wherein the carbon is acid-washed.
3. The process of Claim 1 wherein the carbon is a three-dimensional
matrix carbonaceous material.
- 10 4. The process of Claim 3 wherein the carbon is obtained by
introducing gaseous or vaporous hydrocarbons into a mass of carbon black
granules; decomposing the hydrocarbons to deposit carbon on the surface of the
granules; and treating the resulting material with an activator gas comprising steam
to provide a porous carbonaceous material.
- 15 5. The process of Claim 1 wherein the carbon contains less than about
100 ppm by weight iron.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/17526

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B31/28 B01J21/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9414 Derwent Publications Ltd., London, GB; AN 90-054036 XP002022018 & JP,B,06 029 129 (IDEMITSU PETROCHEM KK) , 20 April 1994 cited in the application see abstract</p> <p style="text-align: center;">--- -/--</p>	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 94, no. 9, 2 March 1981 Columbus, Ohio, US; abstract no. 65095v, page 673; XP002022017 see abstract & JP,B,08 014 044 (MITSUBISHI GAS CHEMICAL CO., INC.) 14 April 1980 ---	1
A	US,A,5 136 113 (V.N.M. RAO) 4 August 1992 cited in the application see column 5, line 31 - line 43; table I ---	2,5
A	GB,A,2 217 701 (VSESOJUZNY NAUCHNO-ISSLEDOVATELSKY INSTITUT TEKNICHESKOGO UGLERODA) 1 November 1989 see abstract; example 1 & US,A,4 978 649 cited in the application ---	3,4
A	EP,A,0 003 530 (STAUFFER CHEMICAL COMPANY) 22 August 1979 & US,A,4 231 959 cited in the application ---	
A	DE,A,33 27 274 (BAYER AG) 7 February 1985 & US,A,4 764 308 cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/17526

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5136113	04-08-92	AU-A- 2398292	23-02-93
		CN-A- 1068810	10-02-93
		DE-D- 69211347	11-07-96
		DE-T- 69211347	05-12-96
		EP-A- 0596007	11-05-94
		ES-T- 2088587	16-08-96
		JP-T- 6509343	20-10-94
		WO-A- 9302029	04-02-93
		ZA-A- 9201883	13-09-93

GB-A-2217701	01-11-89	SU-A- 1706690	23-01-92
		AT-B- 398912	27-02-95
		AT-A- 91189	15-07-94
		BE-A- 1001878	03-04-90
		DE-A- 3912886	02-11-89
		FR-A- 2630101	20-10-89
		JP-A- 2051411	21-02-90
		JP-B- 7017368	01-03-95
		SE-B- 465876	11-11-91
		SE-A- 8901404	20-10-89
		US-A- 4978649	18-12-90

EP-A-3530	22-08-79	US-A- 4231959	04-11-80
		AR-A- 230040	29-02-84
		AU-B- 519336	26-11-81
		AU-A- 4314879	23-08-79
		CA-A- 1118787	23-02-82
		JP-A- 54114494	06-09-79

DE-A-3327274	07-02-85	CA-A- 1236115	03-05-88
		EP-A- 0134506	20-03-85
		JP-C- 1854162	07-07-94
		JP-A- 60042214	06-03-85
		US-A- 4764308	16-08-88
